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Gas-seep related carbonate and barite authigenic mineralization in the northern Gulf of California

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ABSTRACT

Authigenic barite and carbonates (dolomite, high-Mg calcite and aragonite) have been recovered from active gas seep sites of the pull-apart Consag and Wagner basins, the northernmost and shallowest (~225 m deep) active basins in the Gulf of California. This gulf encompasses a transform–spreading ridge transitional plate boundary; while seafloor spreading is known to take place in a few basins of the central and southern gulf, in the northern basins mantle upwelling is only suspected. Despite of their tectonic framework, the studied authigenic deposits show fabrics, minerals and isotope compositions similar to those reported for common gas seeps in passive continental margins and in accretionary active margins, and suggest that methane accompanied by Ba- and Sr-rich basinal cold fluids is released to the seafloor. Authigenic carbonates occur as centimeter-sized concretions scattered within silty sands. These concretions consist of cryptocrystalline carbonate pervasive cement (high-Mg calcite to dolomite) containing bioclasts in variable amounts. Aragonite forms crack-fill fibrous cement in association to barite. In addition, well-sorted, sandy sediments largely constituted by barite spheroids with subordinate pyrite have been recovered. The $\delta^{13}C_{PDB}$ from carbonates (cements and skeletal grains) has an overall variation of −45.5 to +1.7‰. The $\delta^{18}O_{PDB}$ of carbonates varies from −3.1 to +4.0‰. The cryptocrystalline cement yielded the lowest $\delta^{13}C$, indicating that it formed through the anaerobic oxidation of methane. The highest $\delta^{18}O_{PDB}$ values (>+3.0‰) correspond to this cement. The range of $\delta^{18}O_{SMOW}$ calculated for water (+1.3 to +2.1‰) is compatible with pore fluid compositions of typical deep-water methane seeps. Barite yielded $\delta^{34}S$ from +38.2 to +44.8‰, well above that of sulfate from pore- and seawater (+14.8 to +23.6‰). Barite precipitates within the sediments through mixing of (*a*) reducing, Ba-rich seep fluids, with (*b*) pore-water, containing sulfate residual from microbial reduction. The reaction of sulfate reduction is coupled to the oxidation of methane. Skeletal carbonates (coral and bivalves) yielded the lowest $^{87}Sr/^{86}Sr$ ratios (0.709133–0.709177), so they do not show further influence than that of seawater. Barite from sandy deposits yielded high $^{87}Sr/^{86}Sr$ values (0.709477–0.709698). The source of radiogenic strontium could be the clastic infill of the basins, while an oceanic crust isotopic signature is absent.

1. Introduction

The seafloor seepage of gas (methane and carbon dioxide, plus minor C_2–C_4 hydrocarbons) and sedimentary fluids *s.l.* (brine, oil and fluidized mud) has been described worldwide, both at passive margins and in accretionary as well as at rifted active margins (Robertson, 1996; Milkov, 2000; Dupré et al., 2007; Talukder, 2012 and references therein). Seepage activity gives rise to a variety of seafloor features including mud volcanoes and diapirs, pockmarks, brine pools and authigenic deposits of carbonates or barite (*e.g.*

Abbreviations: AOM, anaerobic oxidation of methane; EDS, energy dispersive X-ray spectrometry; EPMA, electron probe microanalyzer; GC, Gulf of California; HMC, high-magnesium calcite; SEM, scanning electron microscope; XRD, X-ray diffraction; WDS, wavelength dispersive spectrometry.

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Dando and Hovland, 1992; Milkov, 2000; Judd, 2004; Milkov et al., 2004; Dupré et al., 2007; Jerosch et al., 2007). Chemosynthetic communities, dependent on methane and/or sulfur, are widespread in seep seafloor environments (MacDonald et al., 1990; Barry et al., 1996; Sibuet and Olu, 1998; Levin, 2005). Hydrogen sulfide and bicarbonate are formed through microbially-mediated anaerobic oxidation of methane (AOM) coupled to sulfate reduction (*e.g.* Aloisi et al., 2000). As a result, authigenic deposits of carbonates (high-magnesium calcite —HMC—, aragonite or dolomite) accompanied by disseminated pyrite develop (*e.g.* Canet et al., 2006). In addition to those from modern seeps, numerous AOM-derived carbonate deposits of Cenozoic and, to a lesser extent, Mesozoic age have been reported (Peckmann and Thiel, 2004 and references therein). Barite precipitation can also take place, but as a consequence of the reaction between barium-rich, reducing seep fluids and sulfate-rich seawater; this process has been invoked as the possible origin for many stratiform barite deposits of Paleozoic age (Torres et al., 2003; Canet et al., submitted for publication).

In many areas, a connection between gas seeps, methane hydrate deposits and sub-seafloor hydrocarbon reservoirs has been established (*e.g.* Macgregor, 1993; Collett and Kuuskraa, 1998). Thus, the occurrence of gas-related authigenic deposits on the seafloor may be a key exploration criterion for buried hydrocarbon reservoirs (Pacheco-Muñoz et al., 2005), which has been supported by results obtained for instance in the South China Sea (Chen et al., 2005).

In the Consag and Wagner basins — the shallowest and northernmost active basins in the Gulf of California (GC) — Canet et al. (2010) reported massive gas venting at water depths of ~65–150 m below sea level (bsl) (Fig. 1). Large-scale gas seepage and fluid ejection features were found roughly along the inferred trace of the NNW listric Wagner Fault, and included ~250 gas vents, numerous pockmarks, possible mud volcanoes, and pyrite- and barite-rich sediments. Although these authors (*op. cit.*) did not sample and analyze the gas, they suggested, based on the tectono-sedimentary setting and by analogy with other onshore and offshore manifestations in and nearby the GC, that it could be carbon dioxide- and methane-rich.

The GC is an oblique rift (*i.e.* a system of extensional basins along major, continental transform faults) that presently encompasses the transition between the spreading East Pacific Rise to the south and the right-lateral transform motion of the Cerro Prieto and San Andreas fault systems to the north (Fig. 1). There are eight tectonically active basins in the GC, of which three have been found to undergo seafloor spreading (Lizarralde et al., 2007). Among them, the Guaymas basin in the central GC is the most studied, given that active seafloor hydrothermal vent systems were discovered there (*e.g.* Gieskes et al., 1982). In this regard, mantle upwelling in the northern GC has been suggested in relation to a suspected, nascent spreading center (Wang et al., 2009).

The basins in the GC are heavily sedimented; in particular, in the northern GC a basin infill sequence of at least 5 km thick has been syntectonically deposited (Pérez, 1980) and the sediment rate is of 3.77 cm yr^{-1} (measured in the Upper Delfín basin by Baba et al., 1991). Leaving aside that sedimentation might be hindering the rise of magma related to seafloor spreading (Einsele, 1985), such a thick sedimentary sequence being affected by high heat flow could be an important source of methane and associated light hydrocarbons (Lonsdale, 1985), as suggested by the occurrence of seafloor gas vents.

This contribution presents the results of an isotope geochemistry study (sulfur, carbon, oxygen and strontium), along with petrographic and mineralogical data, of carbonate and barite gas seep-related, authigenic deposits from the Wagner and Consag basins, in the framework of the tectonic and sedimentary processes of the GC. The principal goals of this paper are to determine the processes triggering authigenic mineralization and to elucidate the origin and nature of fluids involved in these processes. We also examine the role of microorganisms and the effects of the environmental conditions in the growth of these authigenic deposits.

2. Study area

The GC is approximately 1000 km long and up to 150 km wide, and consists of a series of basins separated by bathymetric sills, becoming shallower toward the north. The Consag and Wagner basins are located toward the northernmost end of the GC, between the Upper GC to the north and the Upper Delfín and Lower Delfín basins to the south (Fig. 1). All these basins are tectonically active (Aragón-Arreola and Martín-Barajas, 2007). With a maximum depth of ~225 m bsl, Consag and Wagner are the shallowest active basins in the GC.

2.1. Tectonic and geological framework

The GC has had a complex evolution since the Middle Miocene (16–12 Ma), when the tectonic regime switched from subduction to rifting (Martín-Barajas and Delgado-Argote, 1995). During the Oligocene the oceanic Farallon Plate subducted under the North America Plate (Atwater, 1970). Subduction along Baja California was deactivated between the Middle Miocene and the Lower Pliocene (between 12 and 5.5 Ma). Subsequently the motion between the Pacific and North American plates developed predominantly along the Tosco-Abreojos right-lateral fault system (Spencer and Normark, 1989; Michaud et al., 2007). The tectonic regime evolved to a NE–SW oblique focused extension that formed the proto-GC (Stock and Hodges, 1989), and the Baja California Peninsula was gradually transferred to the Pacific Plate, establishing a conservative plate boundary inside the continent (Angelier et al., 1981; Stock and Hodges, 1989). In the northern GC marine incursion and sedimentation started during the Middle Miocene (Delgado-Argote et al., 2000). After the transference of the Baja California Peninsula to the Pacific Plate, an oceanic basin opened in the GC and some oceanic crust formed (Martín-Barajas and Delgado-Argote, 1995); hence, since 5 Ma the East Pacific Rise propagated northwards forming small divergent basins interconnected by large dextral-oblique faults, which can be traced up to the San Andreas fault system (Lonsdale, 1989). Currently, the upwelling of basaltic magma thorough soft sediment results in a sill–sediment complex; so the sedimentation rate surpass the spreading rate hindering the rise of magma to the surface (Einsele, 1985, 1986). During the Late Pliocene, strain and subsidence migrated westward, forming the Wagner and Consag pull-apart basins in the northern GC and leaving an abandoned rift margin in the northeastern GC (Aragón-Arreola and Martín-Barajas, 2007). Presently, the motion between the Pacific and North American plates is essentially right-lateral transform (Lonsdale, 1989; DeMets, 1995).

The Consag and Wagner basins are connected and controlled by the NNW listric Wagner Fault, which branches out from the Cerro Prieto transform fault. Subsidence is controlled by shallow fault arrays rooted in the Wagner Fault, and sediments on it show fault propagation folds (Aragón-Arreola and Martín-Barajas, 2007). The Wagner Fault, like the neighboring Cerro Prieto, Tiburón and the Ballenas-Salsipuedes faults, is seismically active (Ness and Lyle, 1991). According to Frez and González (1991), seismic activity is intense within the Wagner and Consag basins, and focal mechanisms are mainly of strike-slip and dip-slip nature, which is consistent with the pull-apart character of the basins.

Prior to its damming, the Colorado River was the most important source of sedimentary material to the northern GC, but, at present, sediments mostly came from (Andrews, 1991; Carriquiry